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Isolations and characterization of highly water-soluble dimeric lanthanide citrate and malate with ethylenediaminetetraacetate

Mao-Long Chen, Song Gao, Zhao-Hui Zhou*

Department of Chemistry, College of Chemistry and Chemical Engineering, State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen, 361005, China, Fax: +86 592 2183047; Tel: +86 592 2184531; E-mail: zhzhou@xmu.edu.cn

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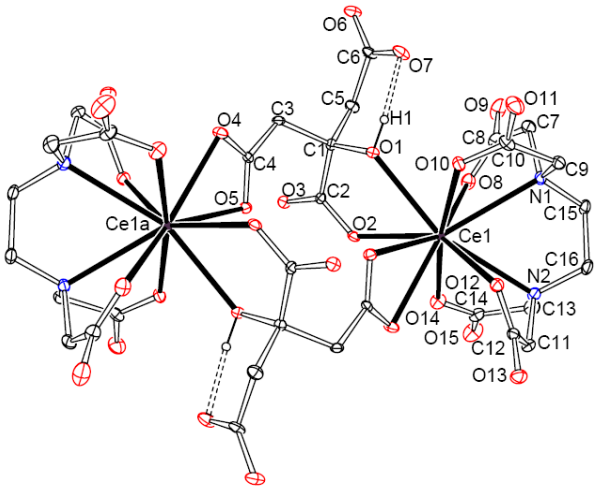

Fig. S1 Anion structure of dimeric complex $(NH_4)_8[Ce_2(Hcit)_2(edta)_2]\cdot 9H_2O$ (**2**)

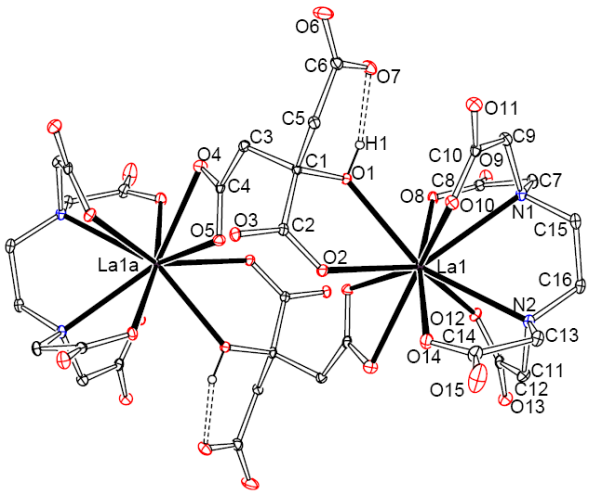

Fig. S2 Anion structure of dimeric complex $K_8[La_2(Hcit)_2(edta)_2]\cdot 16H_2O$ (**3**)

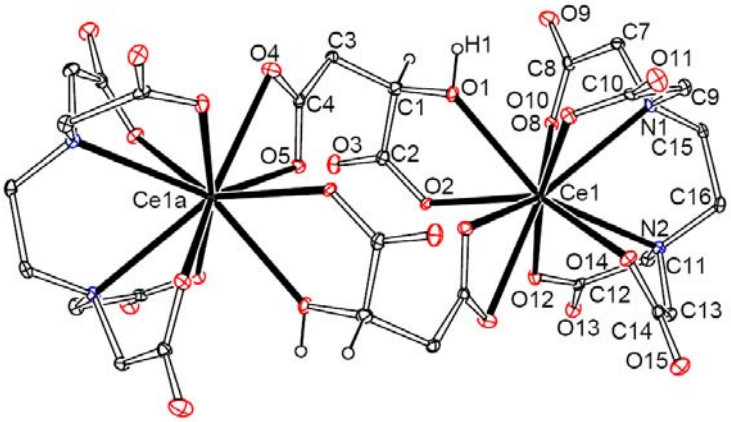

Fig. S3 Anion structure of dimeric complex $K_6[Ce_2(Hmal)_2(edta)_2]\cdot 14H_2O$ (**5**)

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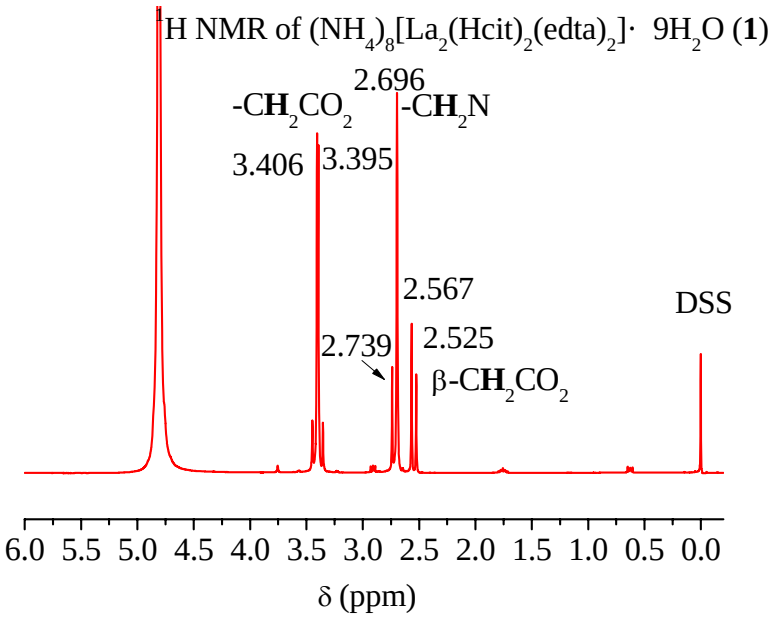

Fig. S4 ^{1}H NMR spectrum of $(NH_4)_8[La_2(Hcit)_2(edta)_2]\cdot 9H_2O$ (**1**)

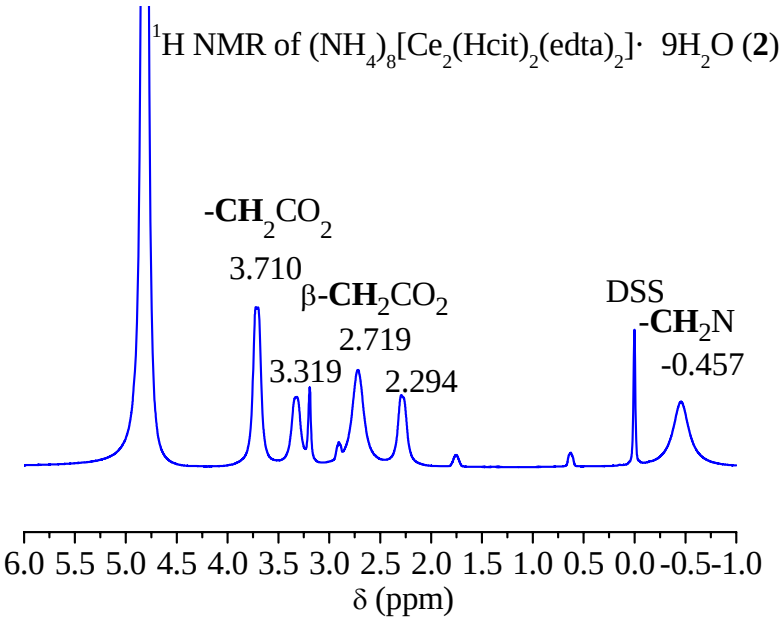

Fig. S5 ^{1}H NMR spectrum of $(NH_4)_8[Ce_2(Hcit)_2(edta)_2]\cdot 9H_2O$ (**2**)

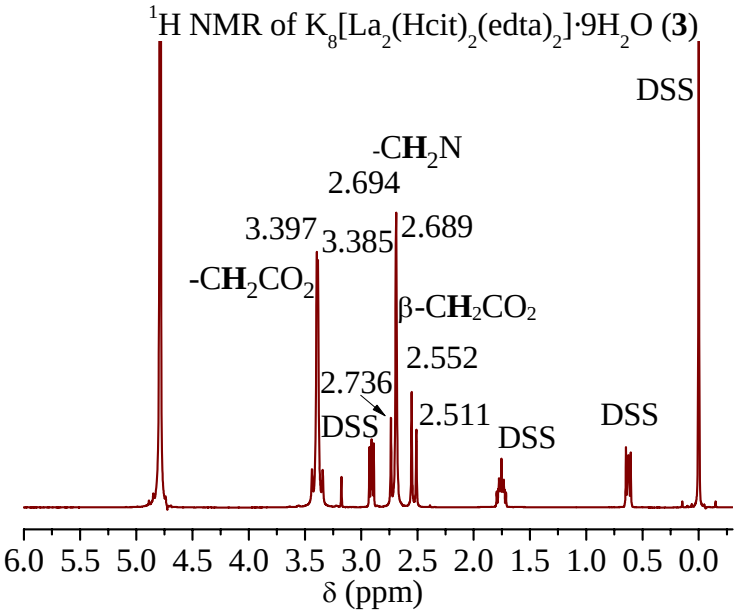

Fig. S6 ^{1}H NMR spectrum of $K_8[La_2(Hcit)_2(edta)_2]\cdot 16H_2O$ (**3**)

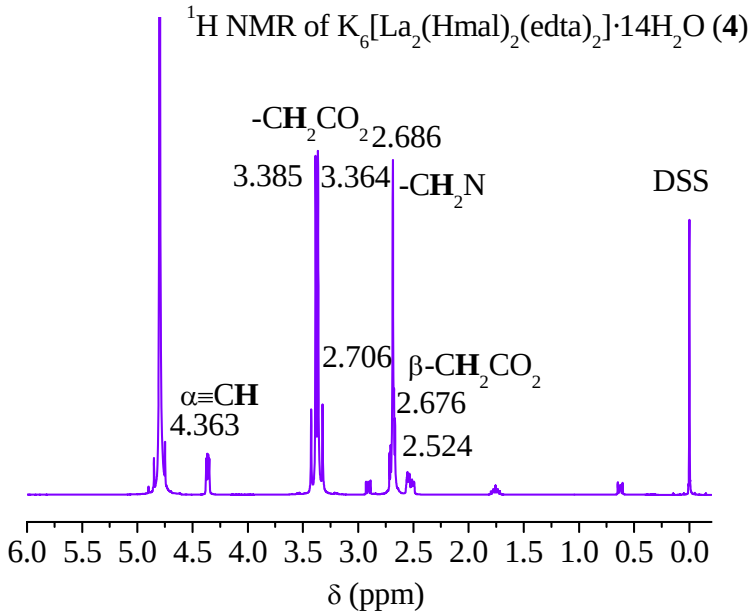

Fig. S7 ^{1}H NMR spectrum of $K_6[La_2(Hmal)_2(edta)_2]\cdot 14H_2O$ (**4**)

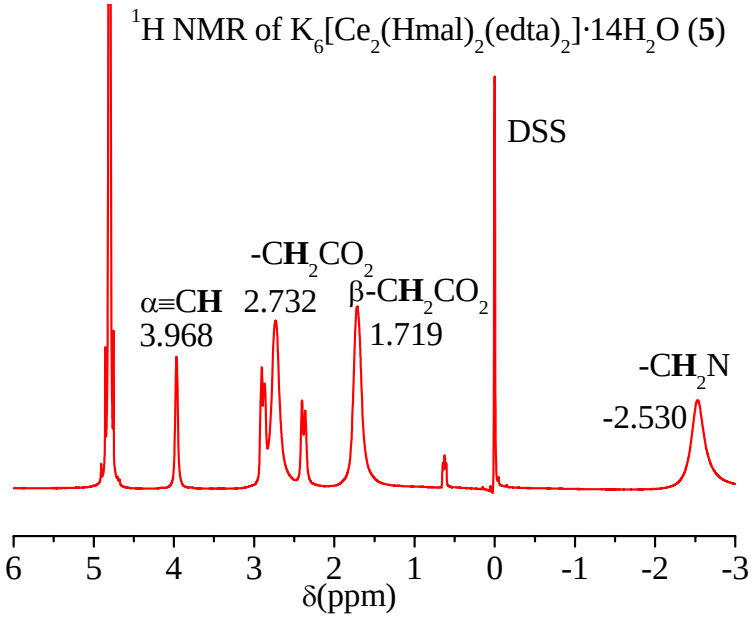

Fig. S8 ^{1}H NMR spectrum of $K_6[Ce_2(Hmal)_2(edta)_2]\cdot 14H_2O$ (**5**)

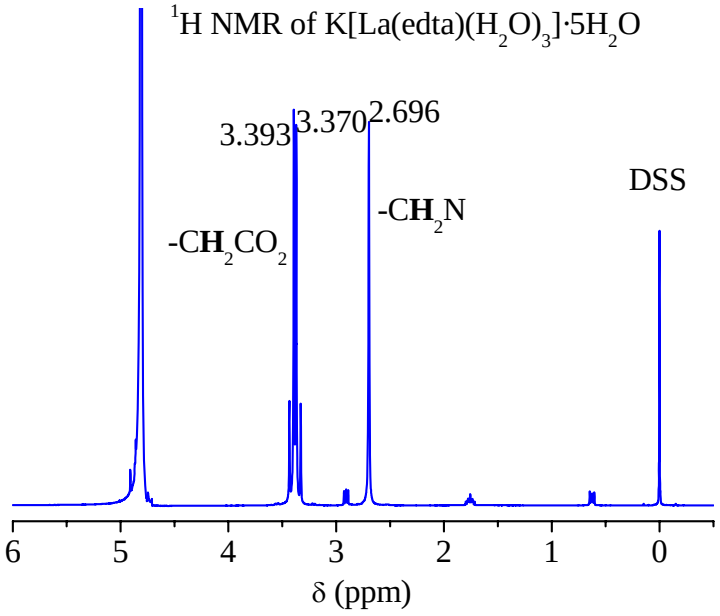

Fig. S9 ^{1}H NMR spectrum of $K[La(edta)(H_2O)_3]\cdot 5H_2O$

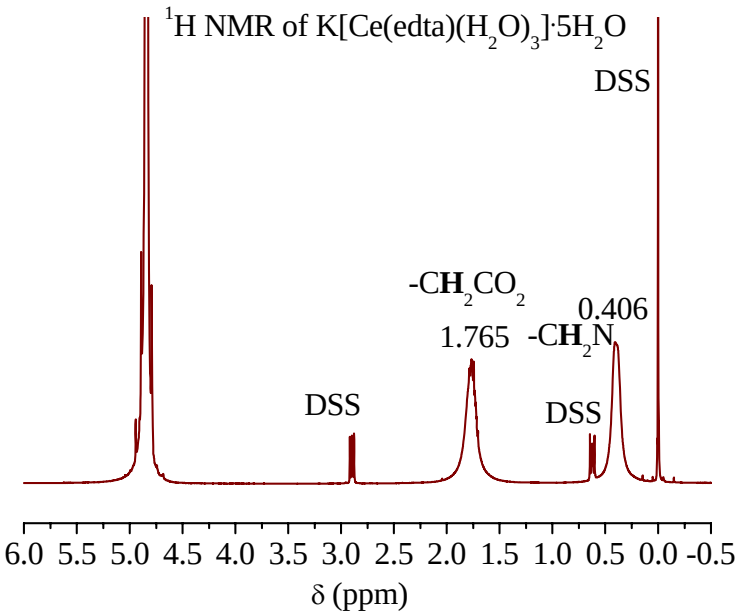

Fig. S10 ^{1}H NMR spectrum of K[Ce(edta)(H$_2$O)$_3$]·5H$_2$O

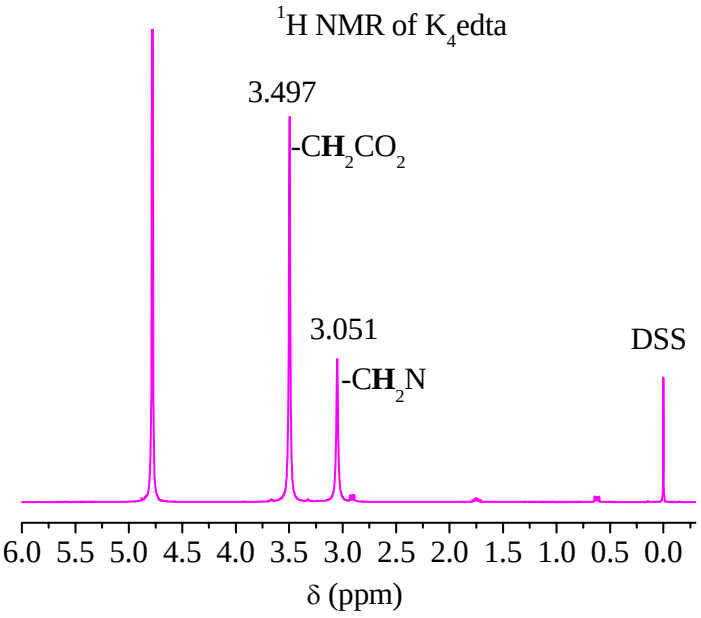

Fig. S11 ^{1}H NMR spectrum of K$_4$edta

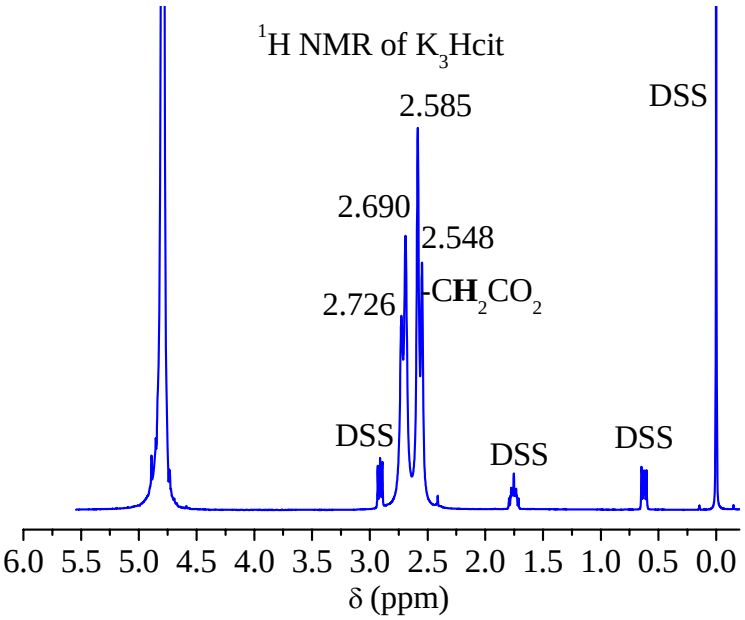

Fig. S12 ^{1}H NMR spectrum of K_3Hcit

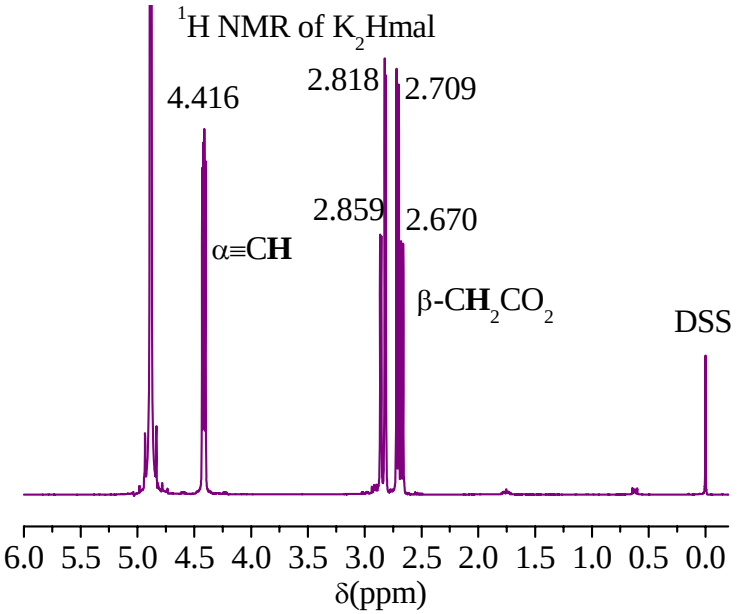

Fig. S13 ^{1}H NMR spectrum of K_2Hmal

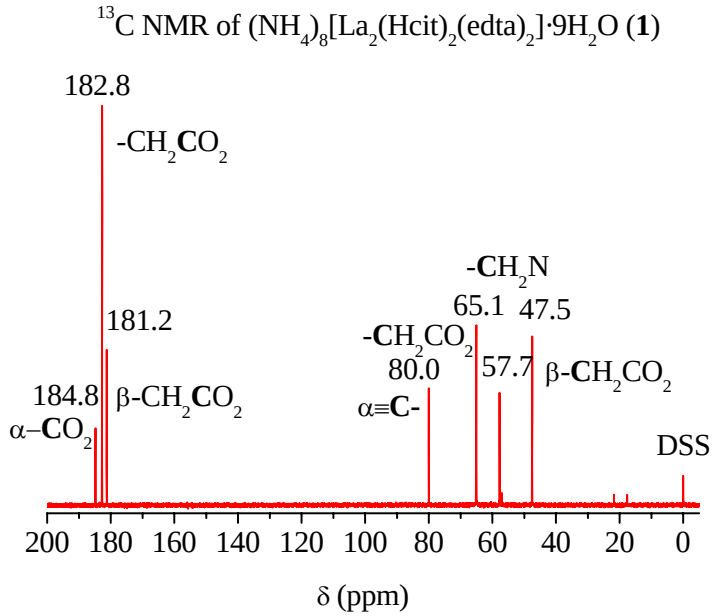

Fig. S14 ^{13}C NMR spectrum of $(NH_4)_8[La_2(Hcit)_2(edta)_2]\cdot 9H_2O$ (**1**)

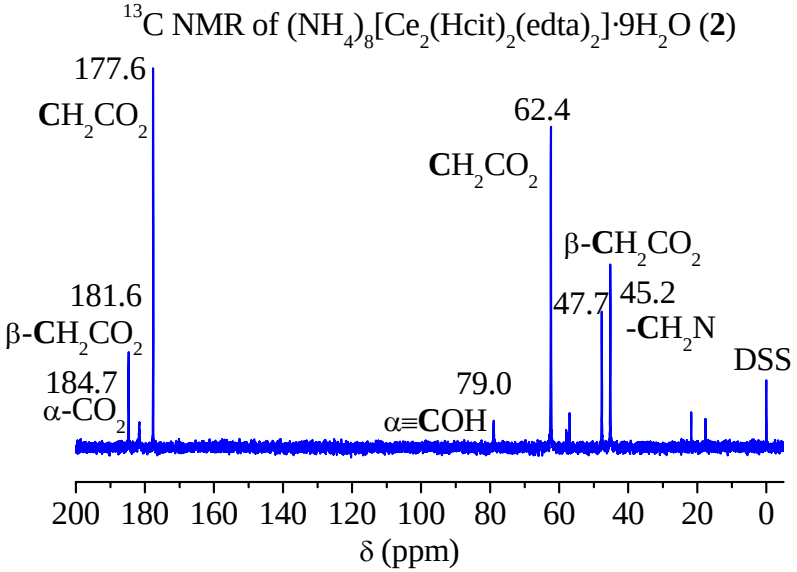

Fig. S15 ^{13}C NMR spectrum of $(NH_4)_8[Ce_2(Hcit)_2(edta)_2]\cdot 9H_2O$ (**2**)

^{13}C NMR of $K_8[La_2(Hcit)_2(edta)_2]\cdot 16H_2O$ (**3**)

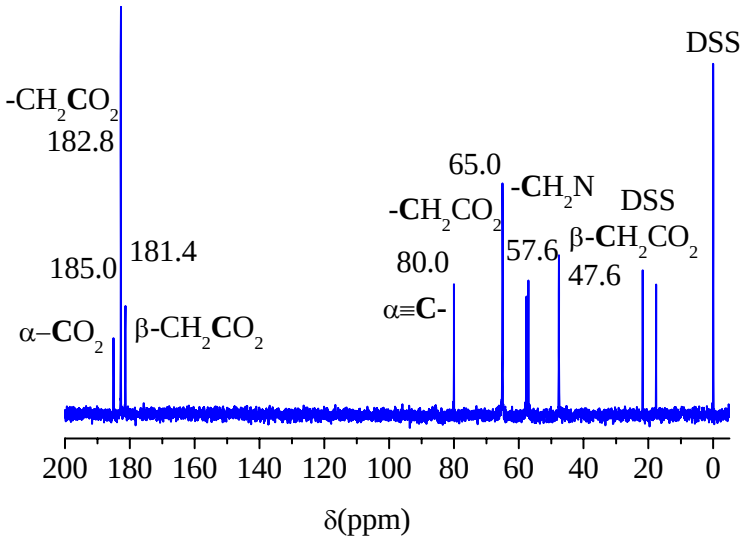

Fig. S16 ^{13}C NMR spectrum of $K_8[La_2(Hcit)_2(edta)_2]\cdot 16H_2O$ (**3**)

^{13}C NMR of $K_6[La_2(Hmal)_2(edta)_2]\cdot 14H_2O$ (**4**)

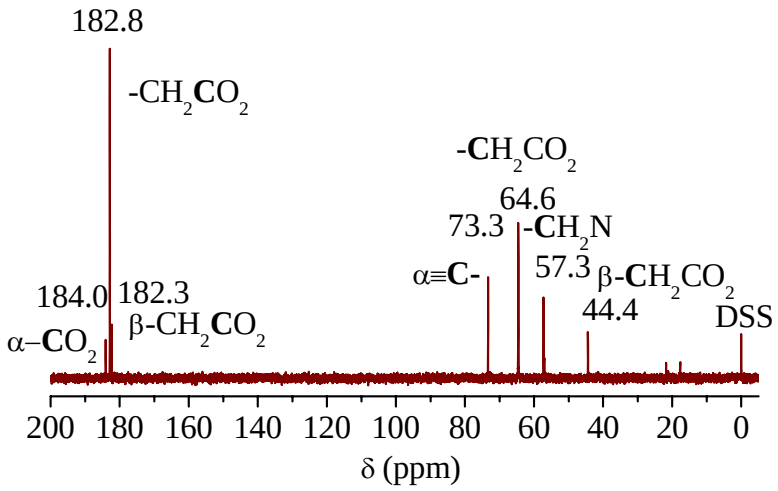

Fig. S17 ^{13}C NMR spectrum of $K_6[La_2(Hmal)_2(edta)_2]\cdot 14H_2O$ (**4**)

^{13}C NMR of $K_6[Ce_2(Hmal)_2(edta)_2]\cdot 14H_2O$ (**5**)

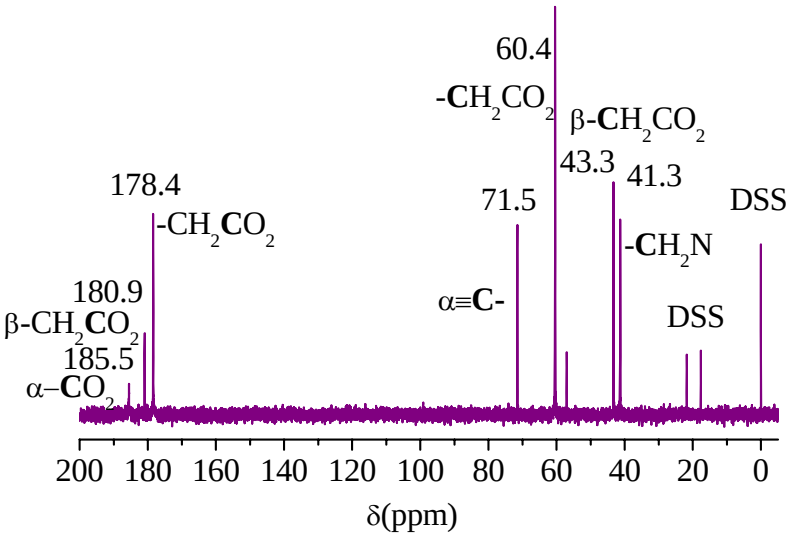

Fig. S18 ^{13}C NMR spectrum of $K_6[Ce_2(Hmal)_2(edta)_2]\cdot 14H_2O$ (**5**)

^{1}H NMR of $K[La(edta)(H_2O)_3]\cdot 5H_2O$

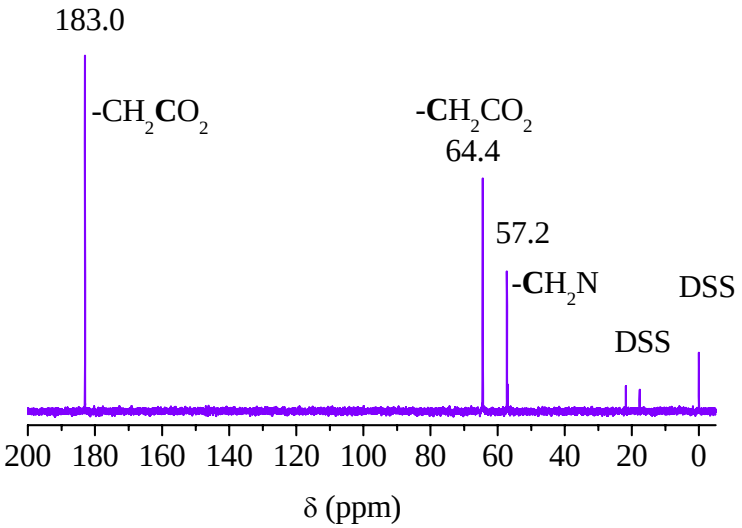

Fig. S19 ^{13}C NMR spectrum of $K[La(edta)(H_2O)_3]\cdot 5H_2O$

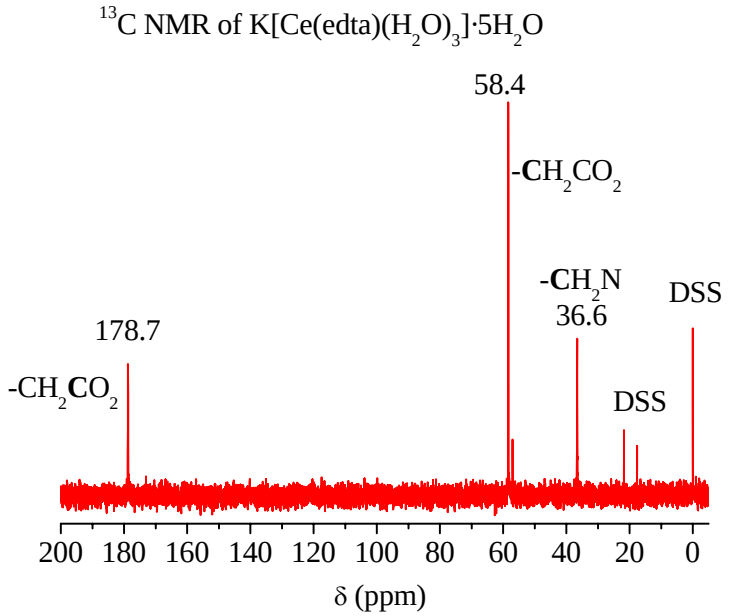

Fig. S20 ^{13}C NMR spectrum of K[Ce(edta)(H$_2$O)$_3$]·5H$_2$O

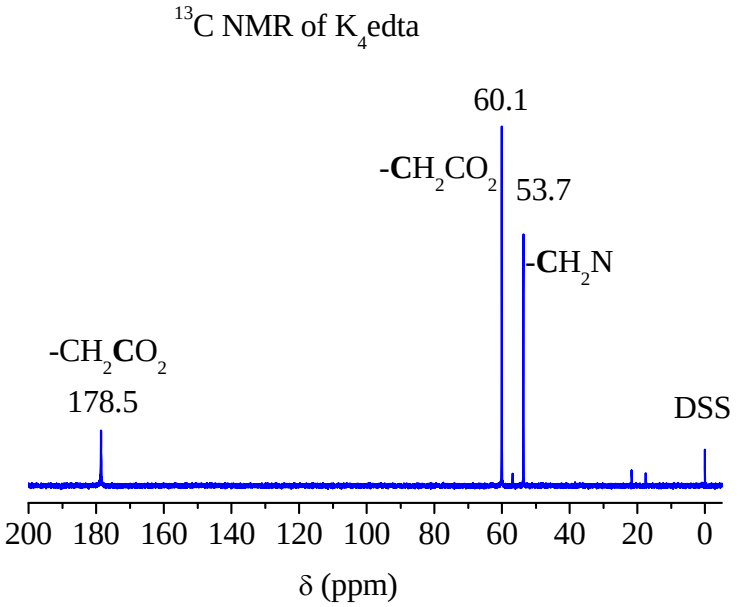

Fig. S21 ^{13}C NMR spectrum of K$_4$edta

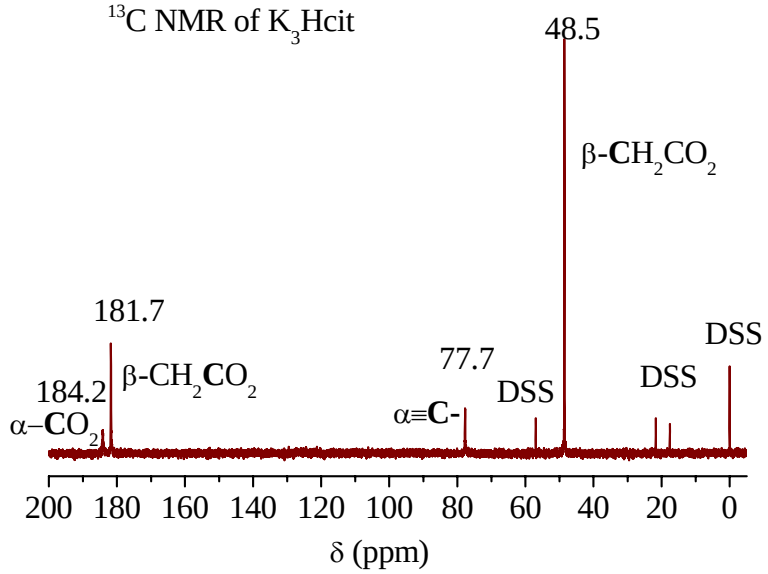

Fig. S22 ^{13}C NMR spectrum of K_3Hcit

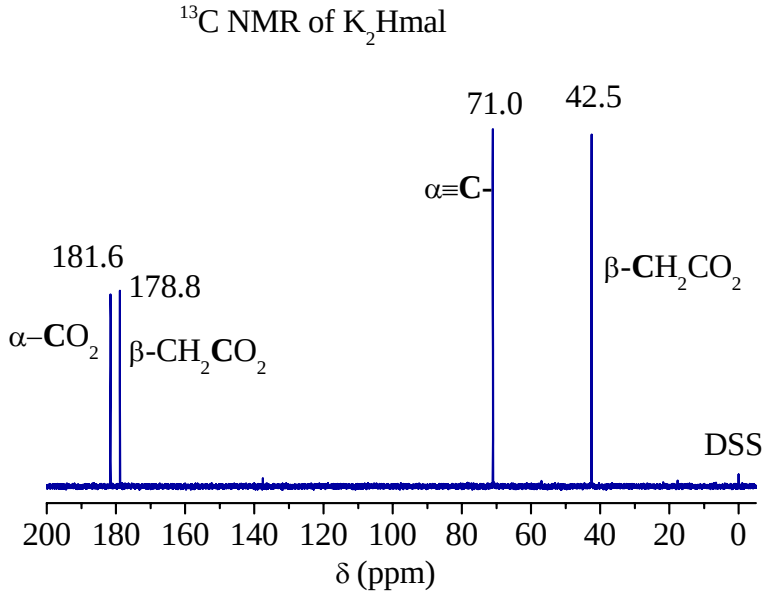

Fig. S23 ^{13}C NMR spectrum of K_2Hmal

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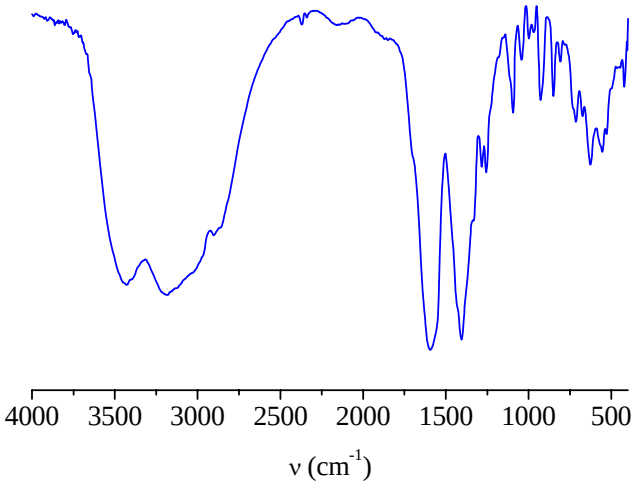

Fig. S24 IR spectrum of $(NH_4)_8[La_2(Hcit)_2(edta)_2]\cdot 9H_2O$ (**1**)

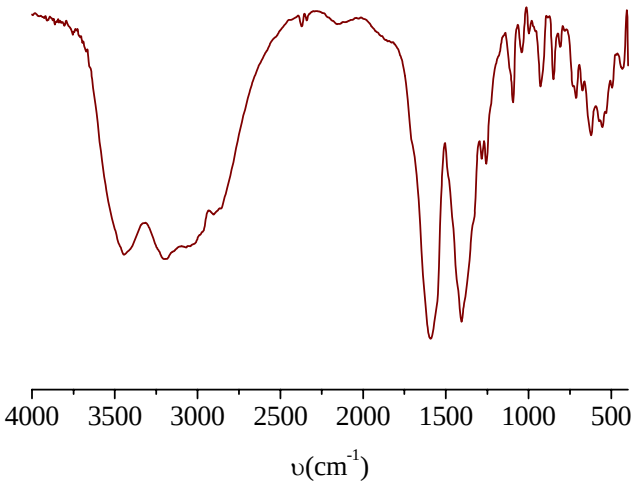

Fig. S25 IR spectrum of $(NH_4)_8[Ce_2(Hcit)_2(edta)_2]\cdot 9H_2O$ (**2**)

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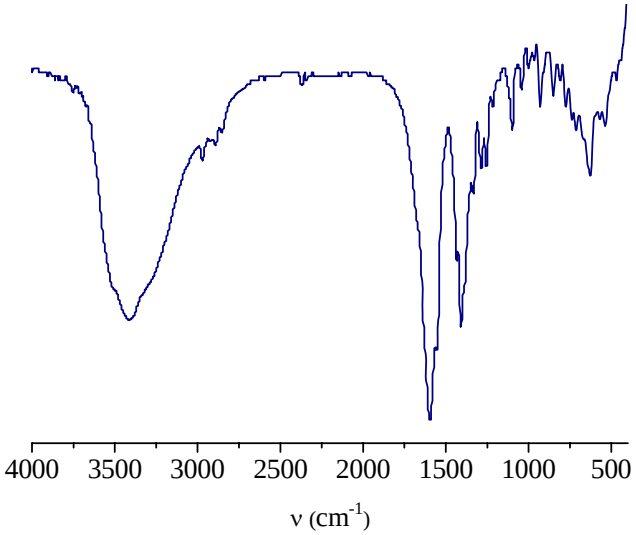

Fig. S26 IR spectrum of $K_8[La_2(Hcit)_2(edta)_2]\cdot 16H_2O$ (**3**)

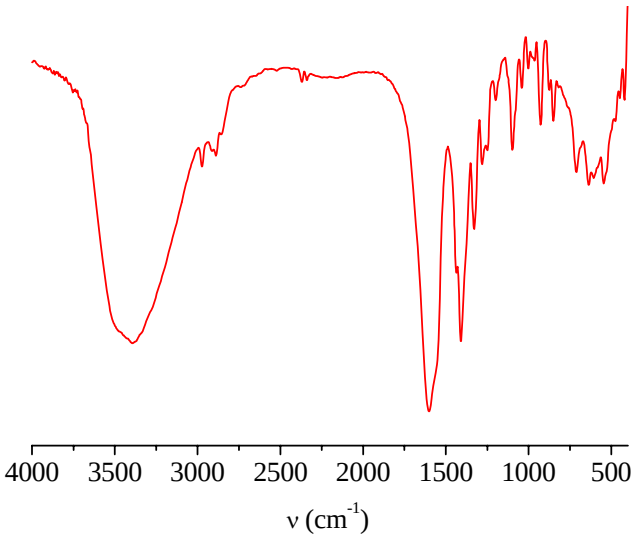

Fig. S27 IR spectrum of $K_6[La_2(Hmal)_2(edta)_2]\cdot 14H_2O$ (**4**)

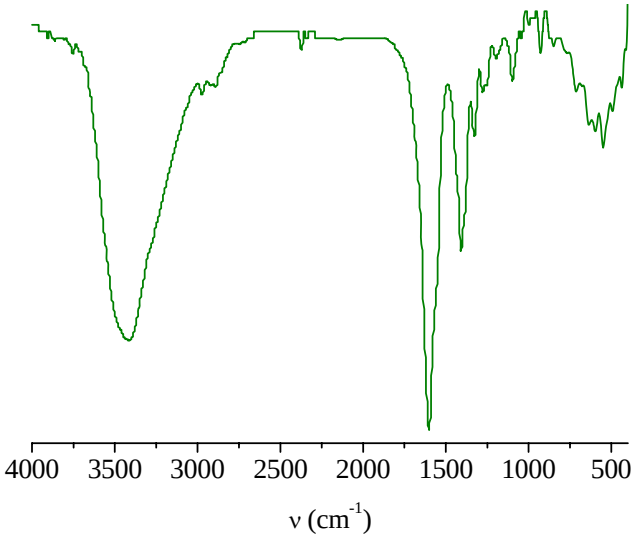

Fig. S28 IR spectrum of $K_6[La_2(Hmal)_2(edta)_2]\cdot 14H_2O$ (**5**)

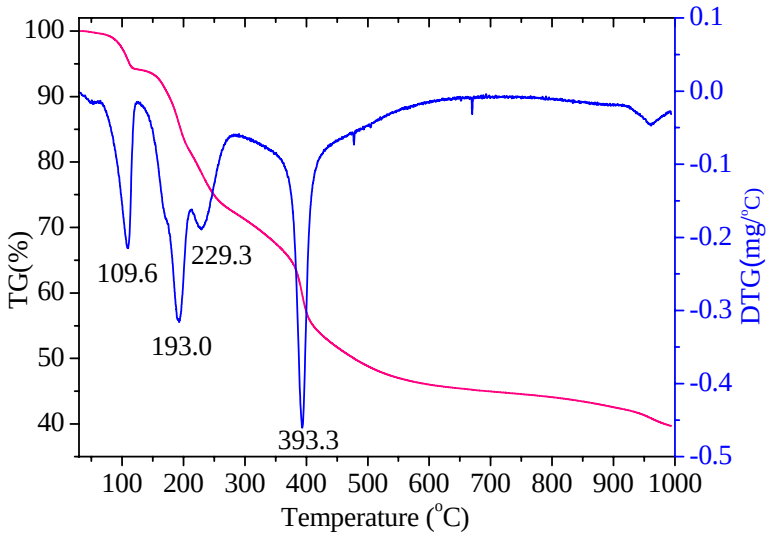

Fig. S29 TG-DTG curve of $(NH_4)_8[La_2(Hcit)_2(edta)_2]\cdot 9H_2O$ (**1**)

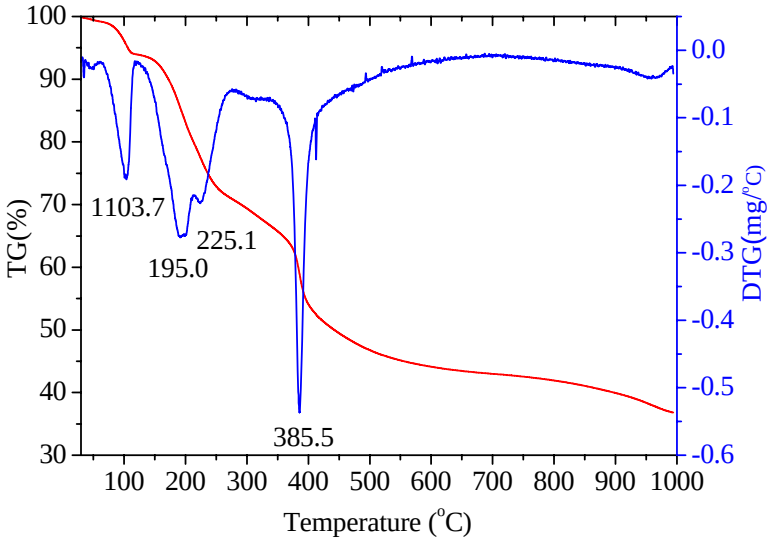

Fig. S30 TG-DTG curve of $(NH_4)_8[Ce_2(Hcit)_2(edta)_2]\cdot 9H_2O$ (**2**)

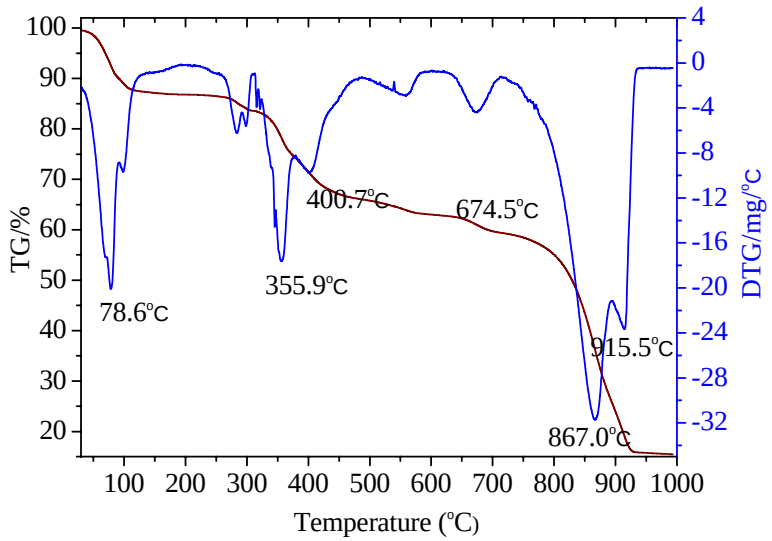

Fig. S31 TG-DTG curve of $K_8[La_2(Hcit)_2(edta)_2]\cdot 16H_2O$ (**3**)

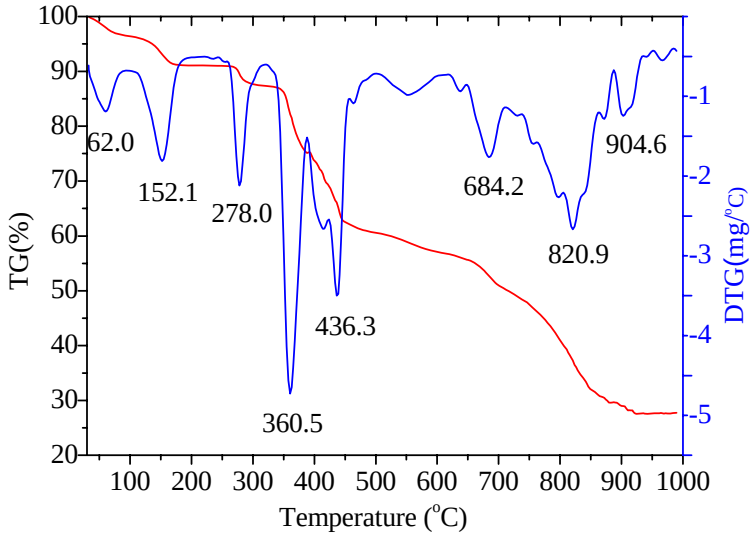

Fig. S32 TG-DTG curve of $K_6[La_2(Hmal)_2(edta)_2]\cdot 14H_2O$ (**4**)

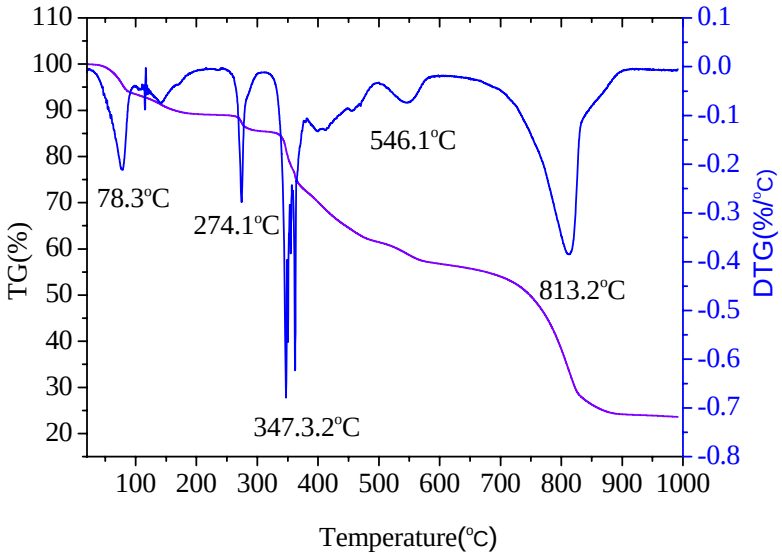

Fig. S33 TG-DTG curve of $K_6[La_2(Hmal)_2(edta)_2]\cdot 14H_2O$(**5**)

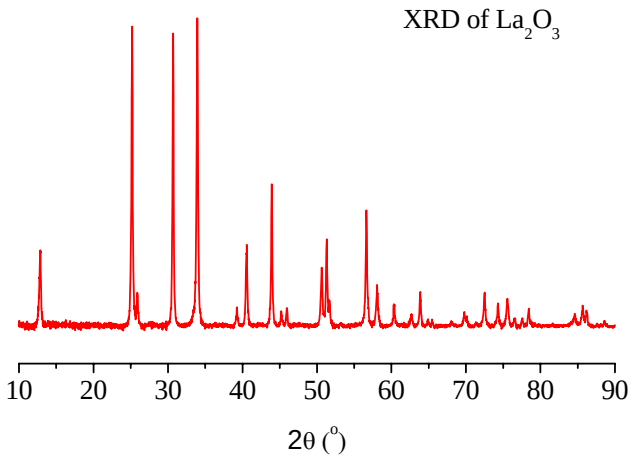

Fig. S34 XRD of La_2O_3

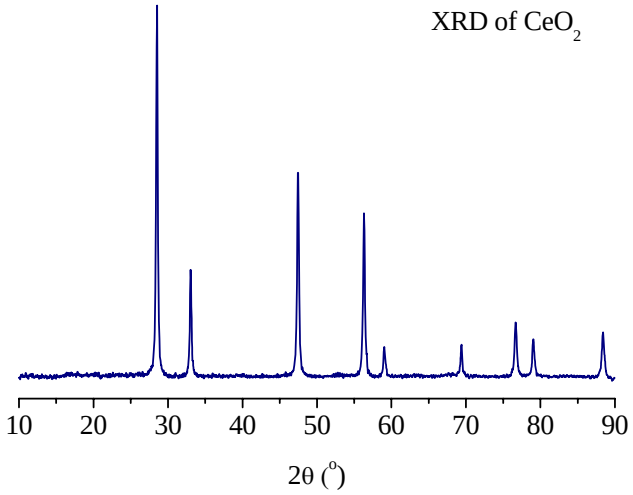

Fig. S35 XRD of CeO_2

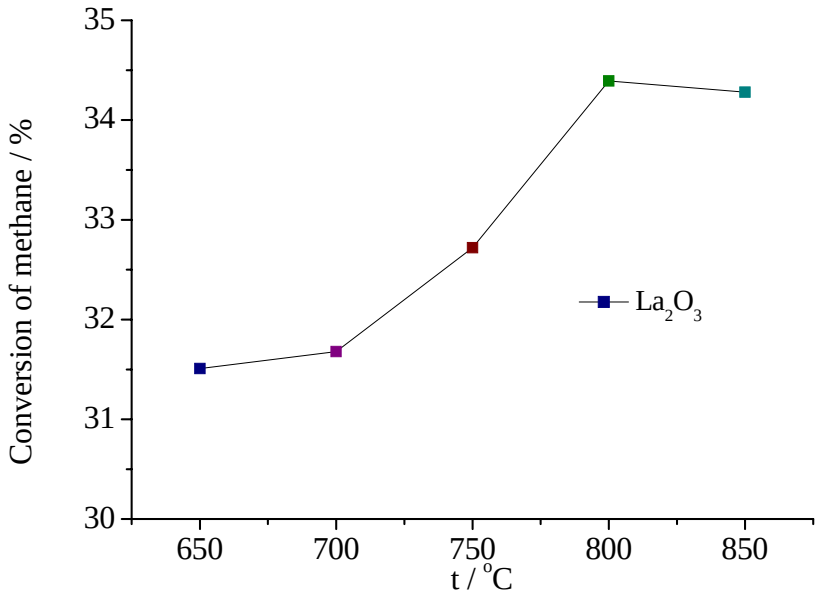

Fig. S36 CH_4 conversions of OCM reaction over La_2O_3
‡: $m_{cat.}$ = 400 mg, n_{CH4}/n_{O2} = 3, GHSV = 7500 h^{-1}

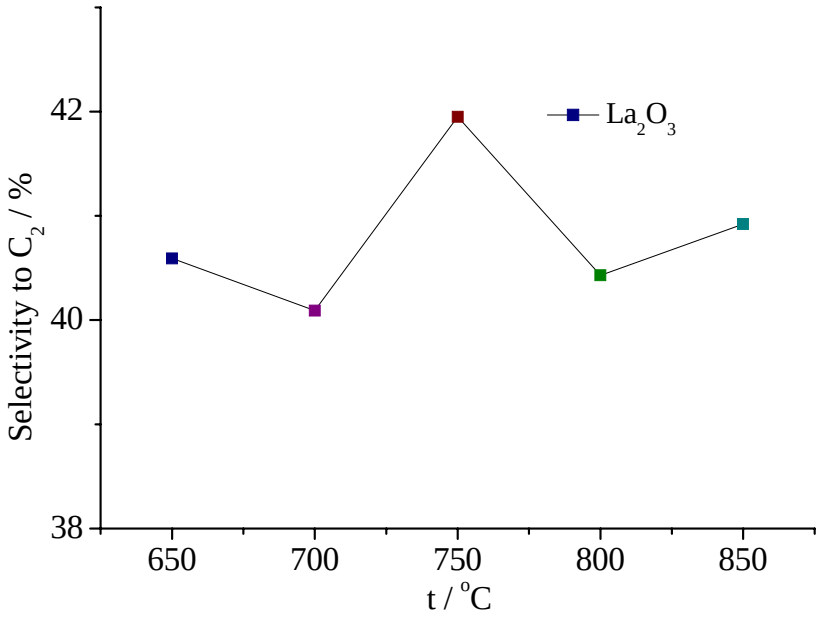

Fig. S37 C_2 selectivity of OCM reaction over La_2O_3
‡: $m_{cat.}$ = 400 mg, n_{CH4}/n_{O2} = 3, GHSV = 7500 h^{-1}

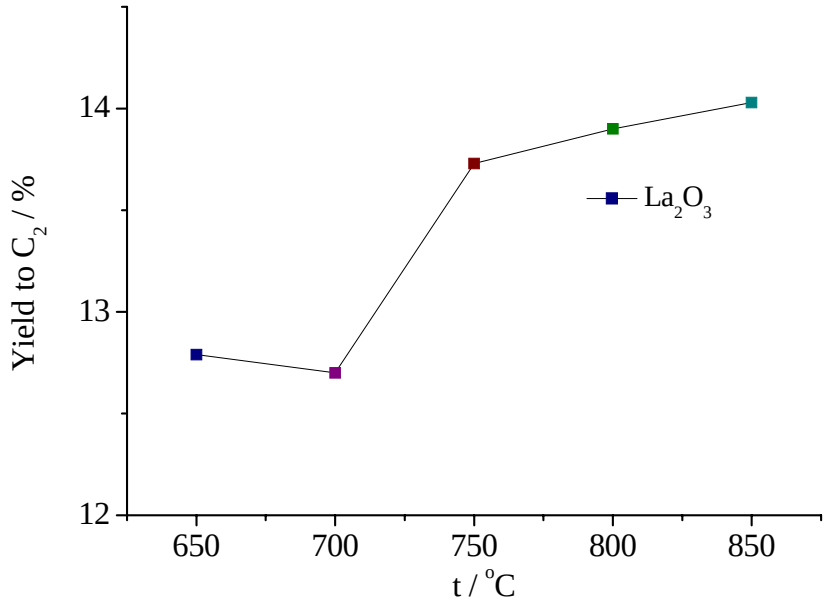

Fig. S37 C_2 yield of OCM reaction over La_2O_3
‡: $m_{cat.}$ = 400 mg, n_{CH4}/n_{O2} = 3, GHSV = 7500 h^{-1}

Table S1 ^{13}C NMR spectral data (in ppm) of complexes **2** and **5**, K_3Hcit, K_4edta, K_2Hmal and $K[Ce(edta)(H_2O)_3]\cdot 5H_2O$ [a]

Compound	α-C	α-CO_2	β-CH_2CO_2	β-CO_2		-CH_2N	-NCH_2CO_2	-CO_2
2	79.0(1.3)	184.7(0.5)	47.7(-0.8)	181.6(-0.1)		45.2(-8.5)	62.4(1.3)	177.6(-0.9)
5	71.5(0.5)	185.5(3.9)	43.3(0.8)	180.9(2.1)		41.3(-12.4)	60.4(0.3)	178.4(-0.1)
$[Hcit]^{3-}$	77.7	184.2	48.5	181.7	$[edta]^{4-}$	53.7	60.1	178.5
$[Hmal]^{2-}$	71.0	181.6	42.5	178.8	$[Ce(edta)(H_2O)_3]^{3-}$	36.6(-17.1)	58.4(-1.7)	178.7(0.2)

[a] △δ values are given in brackets